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910 West Avenue, Austin, Texas 78701 USA

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AQUEOUS INK COMPOSITION

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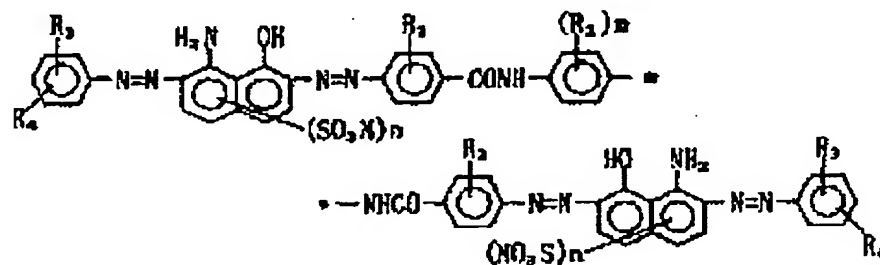
Agents:

Hideoka Komatsu,  
 patent attorney, and 1 other

[Amendments have been incorporated into the text of the translation.]

### Claim

An aqueous ink composition, characterized by including at least one kind of water-soluble dye represented by the following general formula:



$R_1$ : Hydrogen, alkyl group, alkoxy group, halogen, and sulfonic acid group. Where,  $m = 0, 1, \text{ or } 2$ .

$R_2$ : Hydrogen, alkyl group, alkoxy group, and halogen

$R_3, R_4$ : Hydrogen, amino group, nitro group, sulfonic acid group, halogen, alkyl group, carboxyl group, carbamoyl group, sulfamoyl group, and cyano group

$M$ : Cation of hydrogen, sodium, potassium, lithium, organic amine, etc.

$n = 1 \text{ or } 2$ .

## Detailed explanation of the invention

### Technical field

The present invention pertains to an aqueous ink composition suitable for printing, writing tools, recorders, and stamps. In particular, the present invention pertains to a black aqueous ink composition having excellent performances for inkjet printing.

### Prior art

In an inkjet recording, for a good recording for a long time, the ink being used is required to meet the following conditions.

- 1) As ink properties corresponding to a liquid drop generating method and a liquid drop dispersing direction control method, the viscosity, surface tension, specific electric conductivity, and density of the ink should be included in an appropriate range.
- 2) During storage over a long term, use for a long time, or the recording stop, no precipitation should be generated by chemical change, etc., and ink property values should not be changed.
- 3) An image being recorded should have a sufficiently high contrast and should be sharp.
- 4) Drying of a printed image should be fast.

In order to meet the above requirements, it is in demand that the molecular absorption coefficient of a dye used in the ink be sufficiently high and the solubility of the dye in water and a wetting agent be sufficiently high.

Furthermore, for an ink being used in full color printer, etc., the following are in demand.

- 5) A hue with excellent purity should be exhibited.
- 6) Needless to say, the image recorded must be a sharp image with sufficient water resistance, light resistance, and wear resistance without a blur.

In order to meet the above requirements, a number of inks for inkjet recording have been proposed up to now; however, in actuality, inks that sufficiently meet all the above-mentioned conditions have not been obtained yet.

The above required characteristics depend on materials being prescribed in inks, especially dyes, and the development of a new dye has been in demand to meet these requirements.

Usually, an aqueous ink composition is basically composed of a dye and a polyhydric alcohol called a wetting agent or its esters and water, and if necessary, additives such as antimold agents are further included.

As dyes in a conventional black aqueous ink, there are direct dyes and acid dyes such as C.I. direct black-4, -17, -19, -32, -38, -51, -75, -112, -154, etc., and C.I. acid black-1, -2, -7, -24, -28, -94, etc.

However, since the direct dyes above have poor solubility, the image density and the contrast cannot be sufficiently raised by increasing their included concentration.

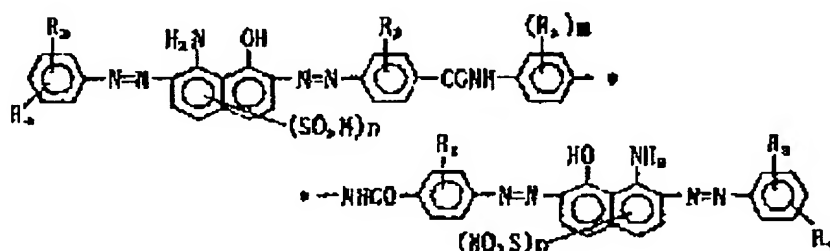
Also, although the acid dyes have good solubility, since the water resistance of the images is inferior, a special processed paper must be used.

### Objective

The objective of the present invention is to provide an aqueous ink composition in which the above-mentioned conventional drawbacks are solved. More specifically, the objective of the present invention is to provide a black aqueous ink with excellent jet characteristics, especially excellent image sharpness, water resistance, and light resistance without clogging.

### Constitution

These inventors used a specific dye as a means to solve the above-mentioned drawbacks, and as a result, it was discovered that it had sufficient effects. Then, the present invention was completed. In other words, the aqueous ink composition of the present invention is characterized by including at least one kind of water-soluble dye represented by the following general formula.



$R_1$ : Hydrogen, alkyl group, alkoxy group, halogen, and sulfonic acid group. Where,  $m = 0, 1, \text{ or } 2$ .

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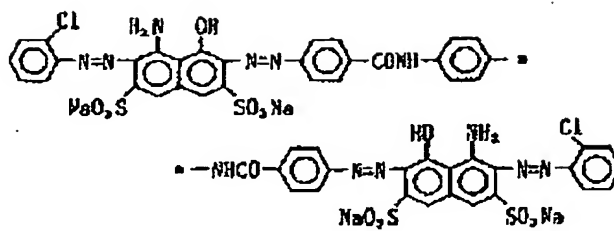
The content of the dye represented by the above-mentioned general formula is 0.5-20 parts by weight, preferably 1.5-6 parts by weight to an ink at 100 parts by weight. If the content is less than 0.5 part by weight, the effect as a colorant is weak, so that the hue of an image being obtained is insufficient. Also, if the content is more than 20 parts by weight,

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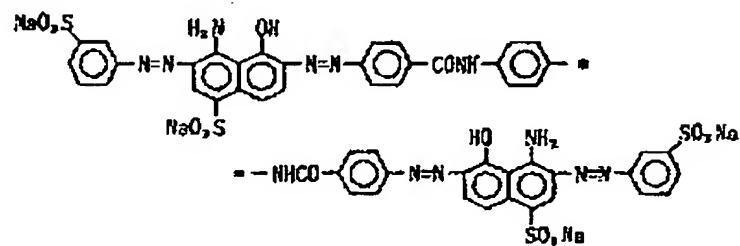
Furthermore, for obtaining a more pure black hue, the dye of the present invention can be used with other red dyes or yellow dyes. As usable dyes, C.I. direct red-1, -9, -11, -37, -62, -75, -83, -99, -220, and -227 and C.I. acid red-87, -92, -94, -115, -131, -154, -186, -254, etc., are mentioned for the red dyes, and C.I. direct yellow-12, -27, -28, -33, -39, -44, -50, -58, -85, -86, -87, -88, -100, -110, -142, and -144 and C.I. acid yellow -7, -17, -23, -29, -42, -99, etc., are mentioned for the yellow dyes.

Next, detailed examples of said dyes are shown.

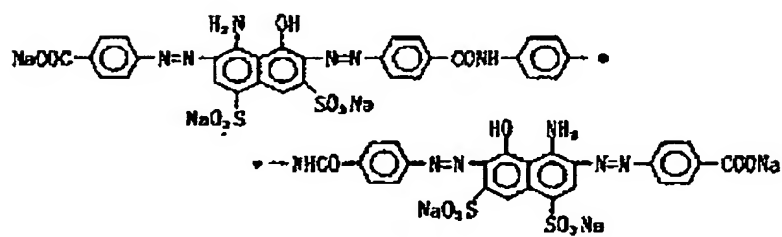
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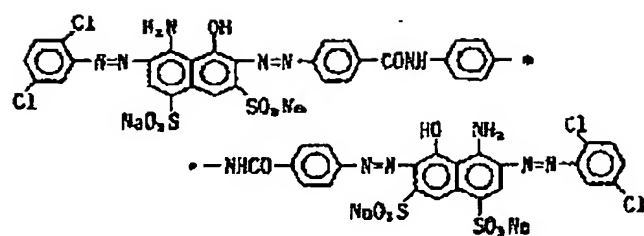
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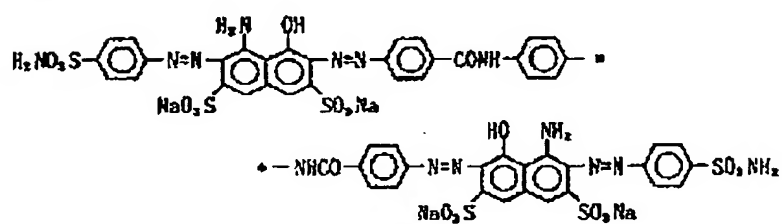
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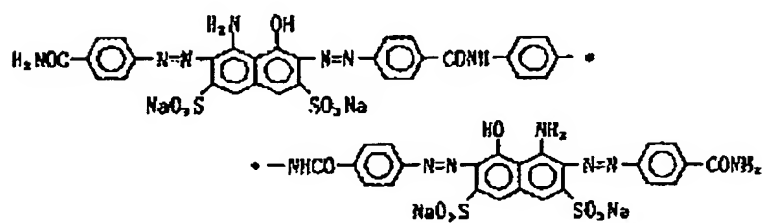
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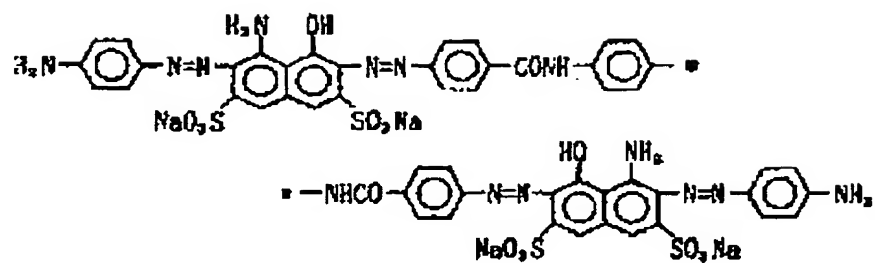


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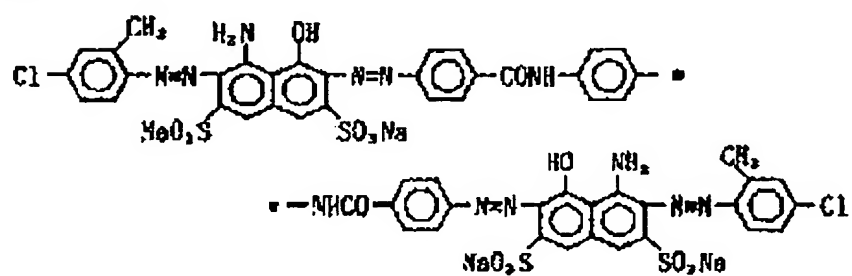




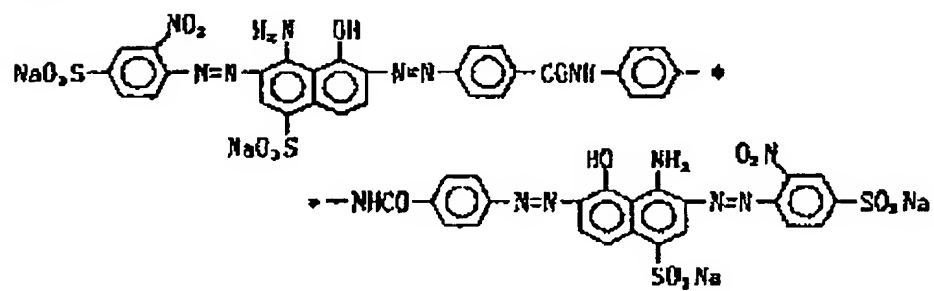
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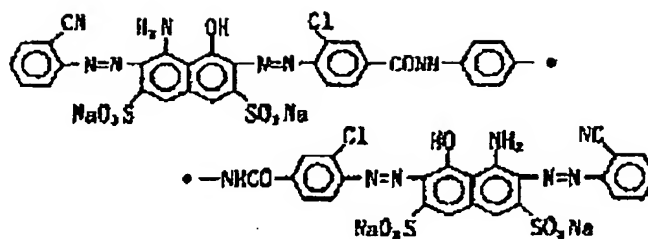
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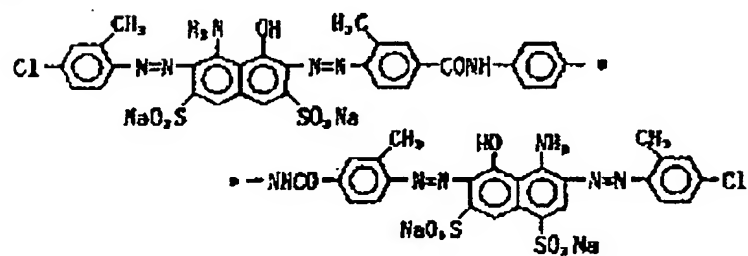
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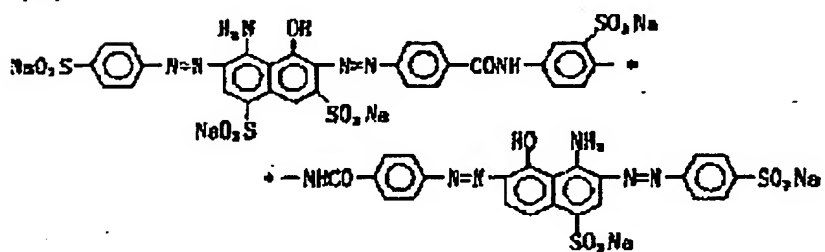
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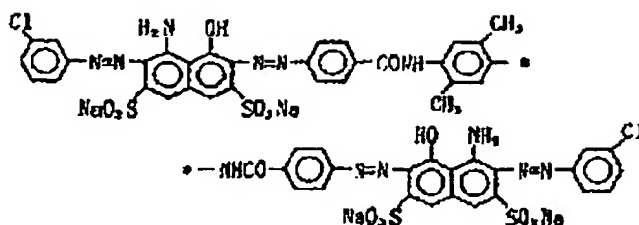
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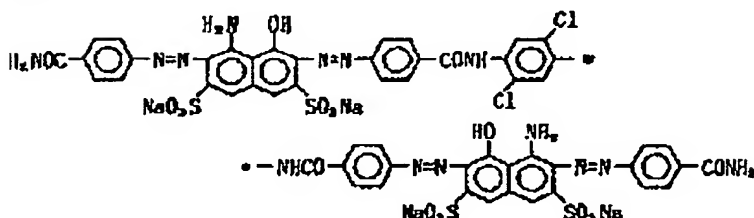
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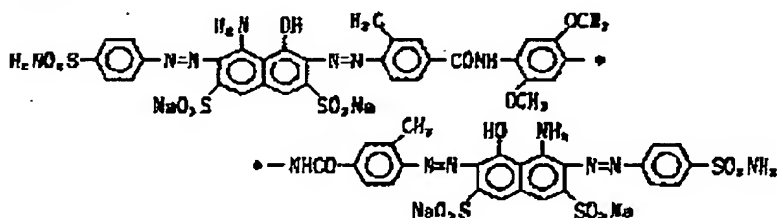
(13)



(14)



(15)



These dyes can be easily synthesized. For example, for the dye shown in the detailed example (1), 2.6 g orthochloroaniline are diazotized by a conventional method and coupling-reacted with 7.2 g H acid at pH 3, so that a red monoazo dye solution is obtained. Next, 3.5 g N,N'-bis(4-aminobenzoyl)paraphenylenediamine is tetrazotized by a conventional method, added to the above monoazo dye with a caustic soda alkalinity, and coupling-reacted. The dye is precipitated by salting out. The yield is 10.8 g.

The ink of the present invention uses water as a solvent component, and in order to adjust the ink properties to desired values, to prevent the ink from being dried, and to improve the solubility of the dye, the following water-soluble organic solvents and water can also be mixed and used.

Polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, and glycerol, alkyl ethers of polyhydric alcohols such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, and triethylene glycol monoethyl ether,

N-methyl-2-pyrrolidone, 2-pyrrolidone, 1,3-dimethylimidazolidinone, dimethyl formaldehyde, triethanolamine, etc.

Among them, diethylene glycol, polyethylene glycol 200-600, triethylene glycol, ethylene glycol, glycerol, and N-methyl-2-pyrrolidone are especially preferable, and a high solubility of the dye and a clogging prevention effect due to moisture vaporization prevention can be obtained by using them.

The content of the above-mentioned water-soluble organic solvent in the ink can be used in a range of 5-80% relative to the total ink weight, and the content is preferably in a range of 10-40% in terms of viscosity, dryness, etc.

In the ink of the present invention, conventional dyes and additives can be added in addition to the above-mentioned dyes and solvents.

As antiseptics and antimold agents, sodium dehydroacetate, sodium sorbitate, 2-pyridinethiol-1-oxide sodium, sodium benzoate, pentachlorophenol sodium, etc., can be used in the present invention.

As a pH adjustor, any substance can be used as long as the pH of the ink can be controlled in a range of 9.0-11.0 without having a negative influence on the ink being prepared.

As its examples, amines such as diethanolamine and triethanolamine, hydroxides of alkali metal elements such as lithium hydroxide, sodium hydroxide, and potassium hydroxide, carbonates of alkali metals such as ammonium hydroxide [sic], lithium carbonate, sodium carbonate, and potassium carbonate, etc., are mentioned.

As a specific electric conductivity adjustor, for example, there are inorganic salts such as potassium chloride, ammonium chloride, sodium sulfate, and sodium carbonate, water-soluble amines such as triethanolamine, etc.

As a chelating agent, for example, there are sodium ethylenediamine tetraacetate, sodium nitrilotriacetate, sodium hydroxyethylethylenediamine triacetate, sodium diethylenetriamine pentaacetate, sodium lauryl diacetate, etc.

As an antirust agent, for example, there are acidic sulfite, sodium thiosulfate, ammonium thioglycollate, diisopropylammonium nitrite, pentaerythritol tetranitrate, dicyclohexylammonium nitrite, etc.

In addition, water-soluble ultraviolet absorbers, water-soluble infrared absorbers, water-soluble high-molecular compounds, dye dissolvers, surfactants, etc., can be added in accordance with the objective.

Next, application examples and comparative examples of the present invention are shown. % is wt%.

Application Example 1

The following composition was heated at about 50°C, stirred and dissolved, and filtered by a Teflon filter with a hole diameter of 0.22  $\mu\text{m}$ , so that an ink was prepared. The properties of said ink are shown in Table 1.

Dye of detailed example (4)	3.0%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Similarly to Application Example 1 except for using materials composed of the following compositions, inks of Application Examples 2-5 and Comparative Examples 1-3 were prepared.

Application Example 2

Dye of detailed example (1)	2.2%
C.I. direct yellow-86	0.8%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Application Example 3

Dye of detailed example (6)	2.3%
C.I. direct yellow-142	0.7%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Application Example 4

Dye of detailed example (9)	1.8%
C.I. direct red 9	0.4%
C.I. direct yellow-28	0.8%
Triethylene glycol	10.0%
2,2'-Thiodiethanol	10.0%
Sodium benzoate	0.2%
Water	76.8%

Application Example 5

Dye of detailed example (14)	1.9%
C.I. direct red 227	0.4%
C.I. direct yellow-144	0.7%
Polyethylene glycol 200	5.0%
Triethylene glycol monomethyl ether	15.0%
Sodium benzoate	0.2%
Water	76.8%

Comparative Example 1

Dye (C.I. direct black 32)	3.0%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Comparative Example 2

Dye (C.I. direct black 51)	3.0%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Comparative Example 3

Dye (C.I. acid black 28)	3.0%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Table 1. Properties of inks

Table 1. Properties of inks				③	④
	pH (25℃)	粘度 (c.p.) (25℃) ①	表面張力 (dyne/cm) (25℃) ②	*1 耐水性 褪色率 (%)	*2 耐光性 褪色率 (%)
⑤ 実施例 1	9.8	2.10	50.0	2.8	5.0
" 2	9.7	2.05	50.5	3.4	5.6
" 3	10.1	2.08	52.5	2.8	3.5
" 4	9.8	2.13	50.8	3.7	4.8
" 5	10.0	2.05	51.5	3.8	3.5
⑥ 比較例 1	9.8	3.50	48.2	6.2	7.0
" 2	10.2	2.82	52.0	7.6	3.7
" 3	10.0	1.95	52.5	20.0	9.5

- Key: 1 Viscosity (c.p.) (25°C)  
 2 Surface tension (dyne/cm) (25°C)  
 3 Water resistance, decolorization rate (%)  
 4 Light resistance, decolorization rate (%)  
 5 Application Example  
 6 Comparative Example

\*1: The ink was diluted to a dye concentration of 1 wt% by pure water, spread on a free sheet by a doctor blade, and dried for 1 day with air, so that a sample was prepared. The sample was immersed for 1 min in water at 30°C, and the concentration was measured by a Macbeth densitometer. It was compared with the concentration before immersing.

Decolorization rate: ((concentration before immersing – concentration after immersing)/concentration before immersing) x 100

\*2: A sample prepared similarly to \*1 was applied to a Fade-o-meter (carbon arc lamp, 63°C) for 3 h, and the decolorization rate was attained by the same method as \*1.

## Effect

(I) For the ink composition of Application Example 1, four items were evaluated and tested. The results are as follows.

### 1) Image sharpness and image dryness:

When the ink was jet-recorded on a free sheet on the market under the condition of a particle frequency of 1100 kHz from a nozzle with an inner diameter of 30 μm, a sharp black image without a blur was obtained. The drying time of the recorded matter was within 10 sec at normal temperature and normal humidity.

### 2) Preservation

The ink was sealed in a glass container and stored at -20°C for 1 month, 4°C for 1 month, at 20°C for 1 year, and 90°C for 1 week, respectively. No precipitation was recognized. Also, no change was recognized in the ink properties and the hue.

### 3) Jet stability

The jet recording of the above-mentioned 1) was continuously carried out for 1000 h; however, no change was shown in nozzle clogging and the jetting direction. A stable recording could be carried out.

### 4) Jet responsivity

After jet recording according to the above-mentioned 1), the ink was held at normal temperature and normal humidity for 1 month, at 40°C and 30% RH for 1 week, and the jet recording of 1) was carried out again. Similarly to the above-mentioned 3), a stable recording could be carried out.

(II) For the inks of Application Examples 2-5, the jet responsivity was tested in the same manner as that of Application Example 1. Good results similar to those of Application Example 1 were obtained. On the contrary, in Comparative Examples 1-3, when the inks were held at normal temperature and normal humidity for 1 week and 40°C and 30% RH for 3 days, a partial clogging was caused in each nozzle, and the ink jetting direction was considerably unstable, so that a jet recording was impossible.



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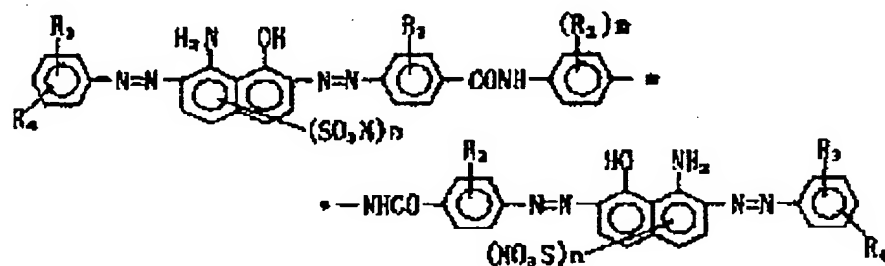
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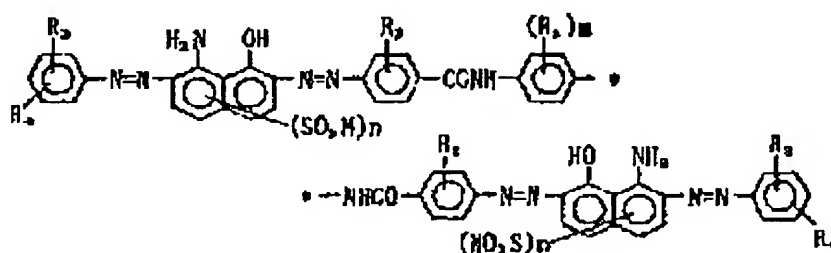
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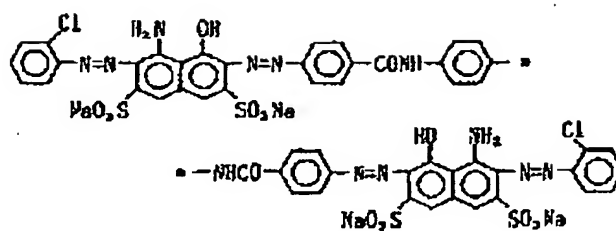
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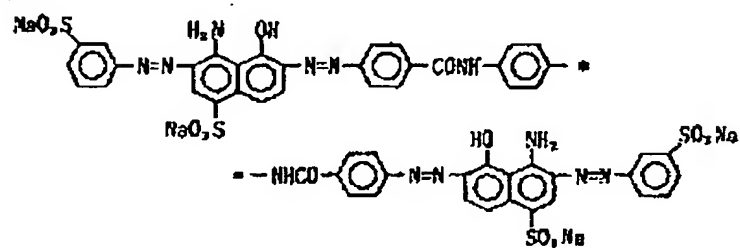
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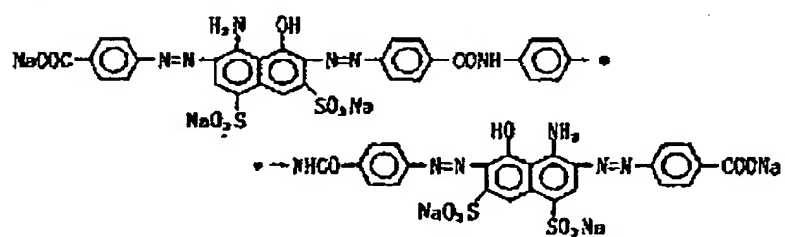
(1)



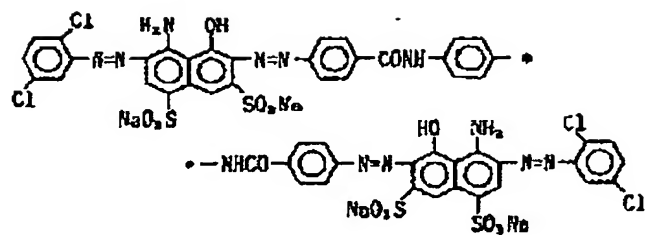
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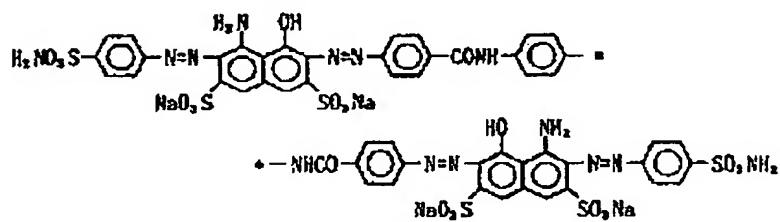
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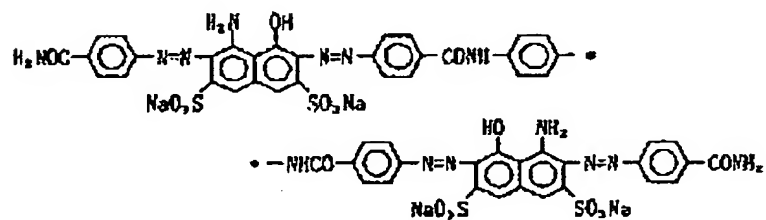
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(8)

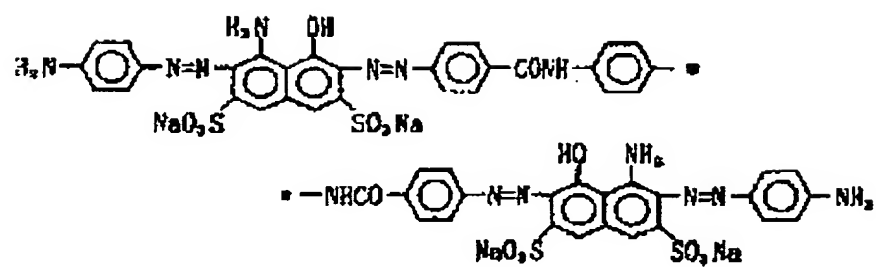


(9)

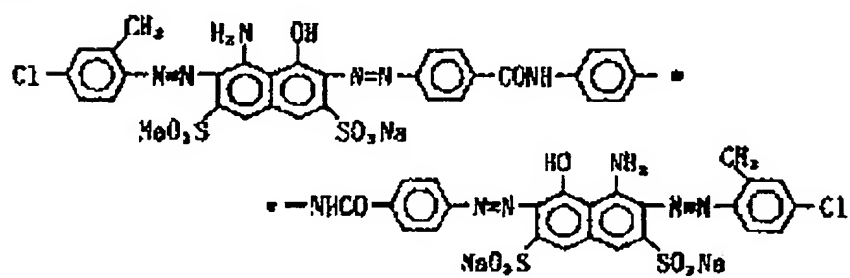




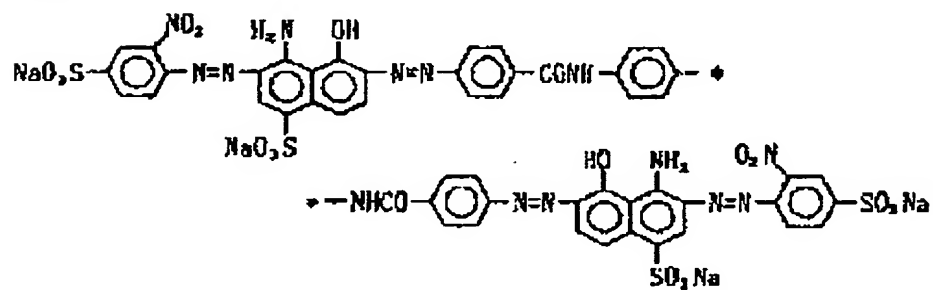
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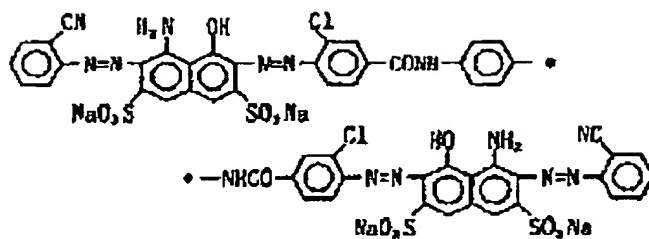
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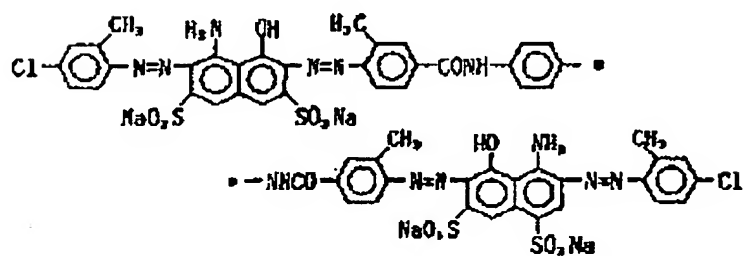
(6)



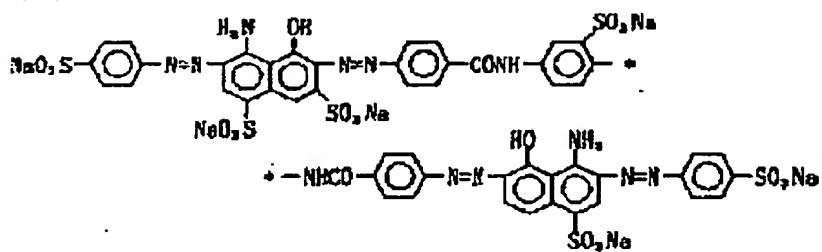
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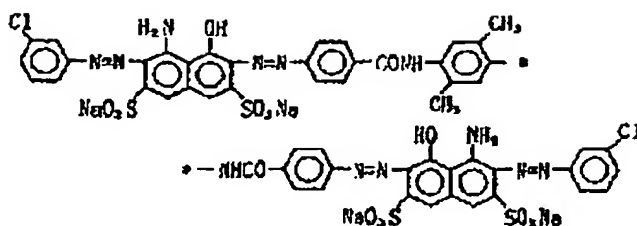
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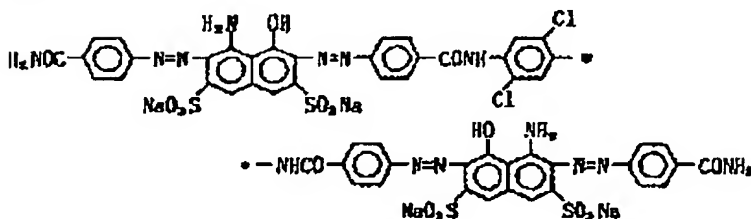
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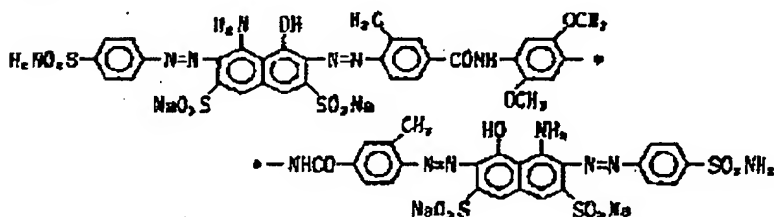
(13)



(14)



(15)



These dyes can be easily synthesized. For example, for the dye shown in the detailed example (1), 2.6 g orthochloroaniline are diazotized by a conventional method and coupling-reacted with 7.2 g H acid at pH 3, so that a red monoazo dye solution is obtained. Next, 3.5 g N,N'-bis(4-aminobenzoyl)paraphenylenediamine is tetrazotized by a conventional method, added to the above monoazo dye with a caustic soda alkalinity, and coupling-reacted. The dye is precipitated by salting out. The yield is 10.8 g.

The ink of the present invention uses water as a solvent component, and in order to adjust the ink properties to desired values, to prevent the ink from being dried, and to improve the solubility of the dye, the following water-soluble organic solvents and water can also be mixed and used.

Polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, and glycerol, alkyl ethers of polyhydric alcohols such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, and triethylene glycol monoethyl ether,

N-methyl-2-pyrrolidone, 2-pyrrolidone, 1,3-dimethylimidazolidinone, dimethyl formaldehyde, triethanolamine, etc.

Among them, diethylene glycol, polyethylene glycol 200-600, triethylene glycol, ethylene glycol, glycerol, and N-methyl-2-pyrrolidone are especially preferable, and a high solubility of the dye and a clogging prevention effect due to moisture vaporization prevention can be obtained by using them.

The content of the above-mentioned water-soluble organic solvent in the ink can be used in a range of 5-80% relative to the total ink weight, and the content is preferably in a range of 10-40% in terms of viscosity, dryness, etc.

In the ink of the present invention, conventional dyes and additives can be added in addition to the above-mentioned dyes and solvents.

As antiseptics and antimold agents, sodium dehydroacetate, sodium sorbitate, 2-pyridinethiol-1-oxide sodium, sodium benzoate, pentachlorophenol sodium, etc., can be used in the present invention.

As a pH adjustor, any substance can be used as long as the pH of the ink can be controlled in a range of 9.0-11.0 without having a negative influence on the ink being prepared.

As its examples, amines such as diethanolamine and triethanolamine, hydroxides of alkali metal elements such as lithium hydroxide, sodium hydroxide, and potassium hydroxide, carbonates of alkali metals such as ammonium hydroxide [sic], lithium carbonate, sodium carbonate, and potassium carbonate, etc., are mentioned.

As a specific electric conductivity adjustor, for example, there are inorganic salts such as potassium chloride, ammonium chloride, sodium sulfate, and sodium carbonate, water-soluble amines such as triethanolamine, etc.

As a chelating agent, for example, there are sodium ethylenediamine tetraacetate, sodium nitrilotriacetate, sodium hydroxyethylethylenediamine triacetate, sodium diethylenetriamine pentaacetate, sodium lauryl diacetate, etc.

As an antirust agent, for example, there are acidic sulfite, sodium thiosulfate, ammonium thioglycollate, diisopropylammonium nitrite, pentaerythritol tetranitrate, dicyclohexylammonium nitrite, etc.

In addition, water-soluble ultraviolet absorbers, water-soluble infrared absorbers, water-soluble high-molecular compounds, dye dissolvers, surfactants, etc., can be added in accordance with the objective.

Next, application examples and comparative examples of the present invention are shown. % is wt%.

Application Example 1

The following composition was heated at about 50°C, stirred and dissolved, and filtered by a Teflon filter with a hole diameter of 0.22  $\mu\text{m}$ , so that an ink was prepared. The properties of said ink are shown in Table 1.

Dye of detailed example (4)	3.0%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Similarly to Application Example 1 except for using materials composed of the following compositions, inks of Application Examples 2-5 and Comparative Examples 1-3 were prepared.

Application Example 2

Dye of detailed example (1)	2.2%
C.I. direct yellow-86	0.8%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Application Example 3

Dye of detailed example (6)	2.3%
C.I. direct yellow-142	0.7%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Application Example 4

Dye of detailed example (9)	1.8%
C.I. direct red 9	0.4%
C.I. direct yellow-28	0.8%
Triethylene glycol	10.0%
2,2'-Thiodiethanol	10.0%
Sodium benzoate	0.2%
Water	76.8%

Application Example 5

Dye of detailed example (14)	1.9%
C.I. direct red 227	0.4%
C.I. direct yellow-144	0.7%
Polyethylene glycol 200	5.0%
Triethylene glycol monomethyl ether	15.0%
Sodium benzoate	0.2%
Water	76.8%

Comparative Example 1

Dye (C.I. direct black 32)	3.0%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Comparative Example 2

Dye (C.I. direct black 51)	3.0%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Comparative Example 3

Dye (C.I. acid black 28)	3.0%
Diethylene glycol	15.0%
Glycerol	5.0%
Sodium dehydroacetate	0.2%
Water	76.8%

Table 1. Properties of inks

Table 1. Properties of inks				③	④
	pH (25℃)	粘度 (c.p.) (25℃) ①	表面張力 (dyne/cm) (25℃) ②	耐水性 褪色率 (%)	耐光性 褪色率 (%)
⑤ 実施例 1	9.8	2.10	50.0	2.8	5.0
" 2	9.7	2.05	50.5	3.4	5.6
" 3	10.1	2.08	52.5	2.8	3.5
" 4	9.8	2.13	50.8	3.7	4.8
" 5	10.0	2.05	51.6	3.8	3.5
⑥ 比較例 1	9.8	3.50	48.2	6.2	7.0
" 2	10.2	2.82	52.0	7.6	3.7
" 3	10.0	1.95	52.5	28.0	9.5

- Key: 1 Viscosity (c.p.) (25°C)  
 2 Surface tension (dyne/cm) (25°C)  
 3 Water resistance, decolorization rate (%)  
 4 Light resistance, decolorization rate (%)  
 5 Application Example  
 6 Comparative Example

\*1: The ink was diluted to a dye concentration of 1 wt% by pure water, spread on a free sheet by a doctor blade, and dried for 1 day with air, so that a sample was prepared. The sample was immersed for 1 min in water at 30°C, and the concentration was measured by a Macbeth densitometer. It was compared with the concentration before immersing.

Decolorization rate: ((concentration before immersing – concentration after immersing)/concentration before immersing) x 100

\*2: A sample prepared similarly to \*1 was applied to a Fade-o-meter (carbon arc lamp, 63°C) for 3 h, and the decolorization rate was attained by the same method as \*1.

## Effect

(I) For the ink composition of Application Example 1, four items were evaluated and tested. The results are as follows.

### 1) Image sharpness and image dryness:

When the ink was jet-recorded on a free sheet on the market under the condition of a particle frequency of 1100 kHz from a nozzle with an inner diameter of 30 μm, a sharp black image without a blur was obtained. The drying time of the recorded matter was within 10 sec at normal temperature and normal humidity.

### 2) Preservation

The ink was sealed in a glass container and stored at -20°C for 1 month, 4°C for 1 month, at 20°C for 1 year, and 90°C for 1 week, respectively. No precipitation was recognized. Also, no change was recognized in the ink properties and the hue.

### 3) Jet stability

The jet recording of the above-mentioned 1) was continuously carried out for 1000 h; however, no change was shown in nozzle clogging and the jetting direction. A stable recording could be carried out.

### 4) Jet responsivity

After jet recording according to the above-mentioned 1), the ink was held at normal temperature and normal humidity for 1 month, at 40°C and 30% RH for 1 week, and the jet recording of 1) was carried out again. Similarly to the above-mentioned 3), a stable recording could be carried out.

(II) For the inks of Application Examples 2-5, the jet responsivity was tested in the same manner as that of Application Example 1. Good results similar to those of Application Example 1 were obtained. On the contrary, in Comparative Examples 1-3, when the inks were held at normal temperature and normal humidity for 1 week and 40°C and 30% RH for 3 days, a partial clogging was caused in each nozzle, and the ink jetting direction was considerably unstable, so that a jet recording was impossible.



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審査請求 未請求 発明の数 1 (全7頁)

⑮ 発明の名称 水性インク組成物

⑯ 特 願 昭60-224901

⑰ 出 願 昭60(1985)10月11日

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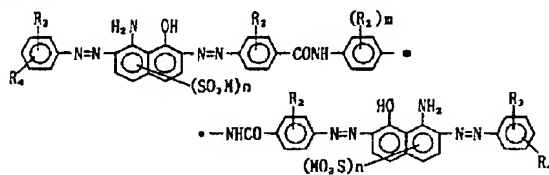
## 明 細 書

### 1. 発 明 の 名 称

水性インク組成物

### 2. 特 許 請 求 の 範 囲

下記一般式で表わされる水溶性染料を少なくとも  
とも一種含有することを特徴とする水性インク  
組成物。



R<sub>1</sub>: 水素、アルキル基、アルコキシ基、

ハロゲン、スルホン酸基、

ここで n = 0、1または2

R<sub>2</sub>: 水素、アルキル基、アルコキシ基、

ハロゲン

R<sub>3</sub>、R<sub>4</sub>: 水素、アミノ基、ニトロ基、

スルホン酸基、ハロゲン、アルキル

基、カルボキシル基、カルバモイル

基、スルファモイル基、シアノ基

M: 水素、ナトリウム、カリウム、リ  
チウム、有機アミン等のカチオンを  
示す。

n = 1 または 2。

### 3. 発 明 の 詳 細 な 説 明

#### 技術分野

本発明は印刷用、筆記具用、記録計用、スタ  
ンプ用として好適な水性インク組成物に関する  
ものであり、特にインクジェット印刷用として  
すぐれた性能を有する黒色水性インク組成物に  
関する。

#### 従来技術

インクジェット記録において、長時間に及ぶ  
て良好な記録を行なうためには、使用するイン  
クが以下の条件を満たすことが必要である。

- 1) 液滴発生方法や液滴飛翔方向制御方法に  
応じたインク物性として、インクの粘度、表面  
張力、比電導度、密度が適正範囲に含まれる  
こと。

2) 長期間保存、長期間使用あるいは記録休止中に化学変化などにより析出が生じたり、インク物性値が変化してはならないこと。

3) 記録される画像が十分にコントラストが高く、鮮明であること。

4) 印字画像の乾燥が速いこと。

以上の要求を満たすためには、インクに使用する染料の分子吸光係数が十分に高いこと、染料の水および湿潤剤に対する溶解度が十分に高いことが要求される。

更にフルカラー・プリンター等に用いられるインクには

5) 純度に関わらず色調を示すこと、

6) 記録された画像は当然のこととして耐水性、耐光性、耐摩耗性に富むニジミのない鮮明な画像でなければならないことが要求される。

以上のような要求を満たすためこれまでに、インクジェット記録用インクとして幾多の提案がなされているが、上記の諸条件のすべてを十分に満足するものはいまだに得られていないの

が現状である。

以上に要求される特性は、インクに処方される材料の中で特に染料により左右されるものであり、これらの要求を満足するために、新規な染料の開発が待たれていた。

通常、水性インク組成物は、基本的には、染料及び湿潤剤といわれる多価アルコールまたはそのエーテル類と水とより構成され、必要に応じてさらに防曇剤等の添加剤を含有するものである。

従来の黒色水性インクにおいて染料としてはC. I. ダイレクトブラック-4、-17、-19、-32、-38、-51、-75、-112、-154等やC. I. アシッドブラック-1、-2、-7、-24、-28、-94等の直接染料や酸性染料がある。

しかしながら、これらの染料のうち直接染料は溶解性が悪いことから、その含有濃度を増大して画像濃度、コントラストを十分に上げることができない。

また酸性染料は溶解性は良いものの特に画像

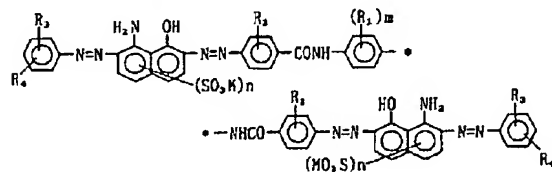
の耐水性に劣るため特殊な加工紙を使用しなければならない。

#### 目 的

本発明は、上記従来の欠点を解決した水性インク組成物を提供するものであり、より詳細には印刷特性がすぐれて目詰まりがなく、特に画像の鮮明性、耐水性、耐光性にすぐれた黒色水性インクを提供するものである。

#### 構 成

本発明者は、上記欠点を解決する手段として特定の染料を用いることが、十分な効果をもたらすことを見い出して、本発明にいたった。すなわち、本発明のインク組成物は、下記一般式で表わされる水溶性染料を少なくとも一種含有することの特徴とするものである。



R<sub>1</sub>: 水素、アルキル基、アルコキシ基、ハロゲン、スルホン酸基、

ここで n = 0, 1 または 2

R<sub>2</sub>: 水素、アルキル基、アルコキシ基、ハロゲン

R<sub>3</sub>, R<sub>4</sub>: 水素、アミノ基、ニトロ基、スルホン酸基、ハロゲン、アルキル基、カルボキシ基、カルバモイル基、スルファモイル基、シアノ基

M: 水素、ナトリウム、カリウム、リチウム、有機アミン等のカチオンを示す。

n = 1 または 2。

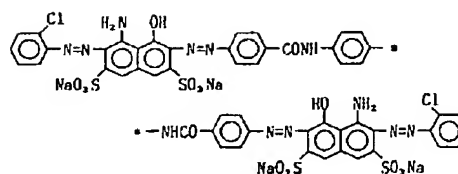
上記一般式で表わされる染料の含有量は、インク 100重量部に対して 0.5~20重量部、好ましくは 1.5~6 重量部が適当である。0.5重量部未満であると着色剤としての効力がうすれて、得られる画像の色調は不十分となり、また20重量部を越えた場合には長時間経時させるとインク中に析出が生じてインクジェット記録が十分

に行なわれなくなる傾向がある。

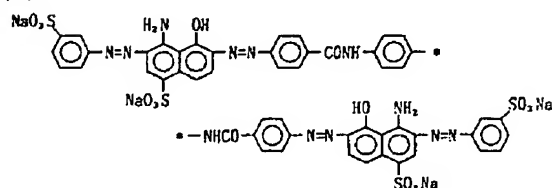
更に色調をより純黒色にするため、本発明の染料と共に他の赤色染料や黄色染料を併用することができる。併用できる染料としては赤色染料ではC. I. ダイレクトレッド-1、-9、-11、-37、-62、-75、-83、-99、-220、-227やC. I. アシッドレッド-87、-92、-94、-115、-131、-154、-186、-254等が、黄色染料ではC. I. ダイレクトイエロー-12、-27、-28、-33、-39、-44、-50、-58、-85、-86、-87、-88、-100、-110、-142、-144やC. I. アシッドイエロー-7、-17、-23、-29、-42、-99等が挙げられる。

以下に該染料の具体例を列挙する。

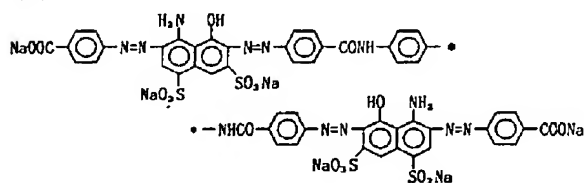
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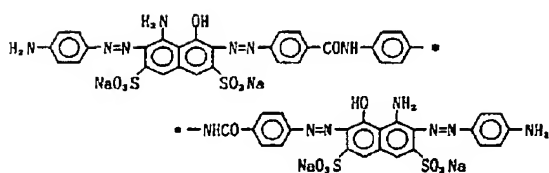
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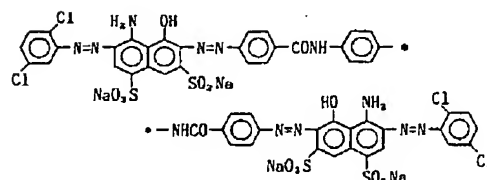
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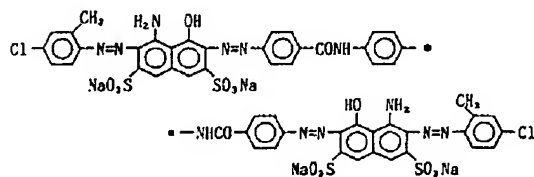
(4)



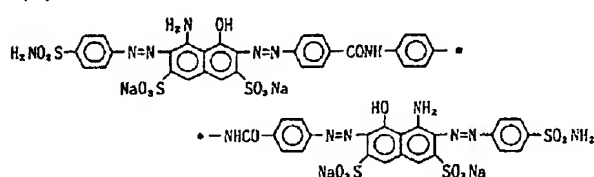
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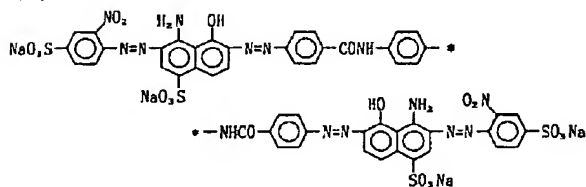
(5)



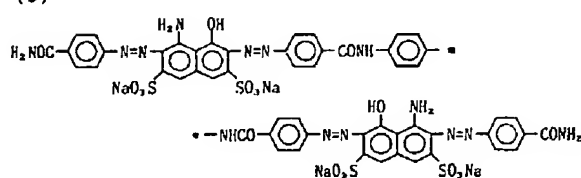
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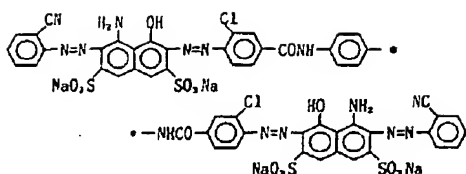
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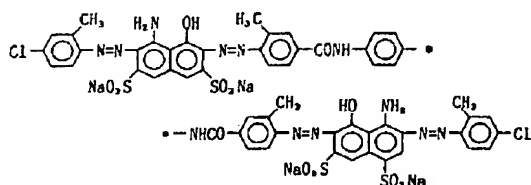
(9)



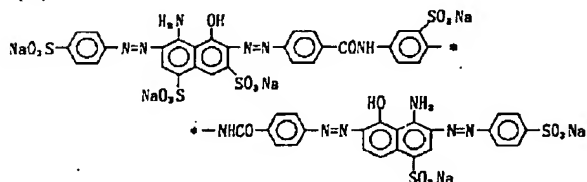
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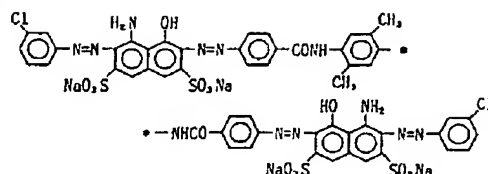
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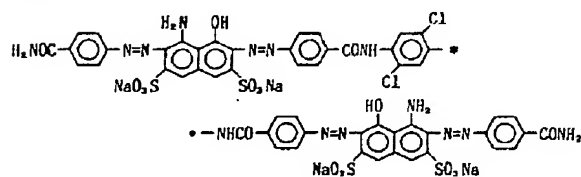
(12)



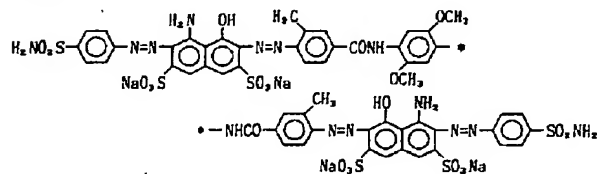
(13)



(14)



(15)



これらの染料は容易に合成することができる。  
例えば具体例(1)で示される染料は 2.6g のオル  
トクロルアニリンを常法でジアゾ化した後、  
pH 3で 7.2g のH酸とカップリング反応して  
赤色のモノアゾ染料液を得る。次に 3.5g の  
N,N'-ビス(4-アミノベンゾイル)パラ  
フェニレンジアミンを常法にてテトラゾ化し、  
苛性ソーダアルカリ性とした先のモノアゾ染料  
溶液に加えてカップリング反応する。終了後塩  
析により染料を析出させる。収量は10.8gであ  
る。

本発明のインクは、溶媒成分として水を使用  
するものであるが、インク物性を所望の値に調  
整するため、インクの乾燥を防止するため、染  
料の溶解性を向上するため等の目的で、下記  
の水溶性有機溶媒と水とを混合して使用するこ  
とができる。

エチレングリコール、ジエチレングリコール、  
トリエチレングリコール、ポリエチレングリ  
コール、ポリプロピレングリコール、グリセリン

等の多価アルコール類、エチレングリコールモ  
ノエチルエーテル、エチレングリコールモノブ  
チルエーテル、ジエチレングリコールモノメチ  
ルエーテル、ジエチレングリコールモノエチル  
エーテル、ジエチレングリコールモノブチルエ  
ーテル、トリエチレングリコールモノメチルエ  
ーテル、トリエチレングリコールモノエチルエ  
ーテル等の多価アルコールのアルキルエーテル  
類、その他、N-メチル-2-ピロリドン、2  
-ピロリドン、1,3-ジメチルイミダゾリジノ  
ン、ジメチルホルムアミド、トリエタノールア  
ミン等である。

これらの中で特に好ましいのはジエチレング  
リコール、ポリエチレングリコール 200~600、  
トリエチレングリコール、エチレングリコール、  
グリセリン、N-メチル-2-ピロリドンであり、  
これらを用いることにより染料の高い溶解  
性と水分蒸発防止による目詰り防止の効果を  
得ることが出来る。

インク中の上記水溶性有機溶媒の含有量はイ

ンク全重量に対して 5~80%の範囲で使用できるが、粘性、乾燥性等から10~40%の範囲で用いることが好ましい。

本発明のインクには上記染料、溶剤の他に従来より知られている染料および添加剤を加えることができる。

防腐防霉剤としては、デヒドロ酢酸ソーダ、ソルビン酸ソーダ、2-ピリジンチオール-1-オキサイドナトリウム、安息香酸ナトリウム、ベンタクロロフェノールナトリウム等が本発明に使用できる。

pH調整剤としては、混合されるインクに悪影響をおよぼさず、インクの pHを 9.0~11.0の範囲に制御できるものであれば任意の物質を使用することができる。

その例として、ジエタノールアミン、トリエタノールアミンなどのアミン、水酸化リチウム、水酸化ナトリウム、水酸化カリウムなどのアルカリ金属元素の水酸化物、水酸化アンモニウム、炭酸リチウム、炭酸ナトリウム、炭酸カリウム

などのアルカリ金属の炭酸塩などがあげられる。

比電気伝導度調整剤としては、例えば、塩化カリウム、塩化アンモニウム、硫酸ナトリウム、炭酸ナトリウムなどの無機塩、トリエタノールアミンなどの水溶性アミンなどがある。

キレート試薬としては、例えば、エチレンジアミン四酢酸ナトリウム、ニトリロ三酢酸ナトリウム、ヒドロキシエチルエチレンジアミン三酢酸ナトリウム、ジエチレントリアミン五酢酸ナトリウム、ラウミル二酢酸ナトリウムなどがある。

防錆剤としては、例えば、酸性亜硫酸塩、チオ硫酸ナトリウム、チオグリコール酸アンモン、ジソプロピルアンモニウムニトライト、四硝酸ペンタエリスリトール、ジシクロヘキシルアンモニウムニトライトなどがある。

その他目的に応じて、水溶性紫外線吸収剤、水溶性赤外線吸収剤、水溶性高分子化合物、染料溶解剤、界面活性剤などを添加することができる。

以下に本発明の実施例および比較例を示す。  
%はすべて重量%である。

#### 実施例 1

下記の組成物を約50℃に加熱して攪拌溶解した後、孔径0.22μmのテフロンフィルターで濾過することによってインクを作成した。該インクの物性は表-1に示すとおりである。

具体例④の染料	3.0%
ジエチレングリコール	15.0%
グリセリン	5.0%
デヒドロ酢酸ナトリウム	0.2%
水	76.8%

下記の組成よりなる材料を用いる以外は実施例1と同様にして、実施例2~5、および比較例1~3のインクを作成した。

#### 実施例 2

具体例①の染料	2.2%
C. I. ダイレクトイエロー86	0.8%
ジエチレングリコール	15.0%
グリセリン	5.0%

デヒドロ酢酸ナトリウム	0.2%
水	76.8%

#### 実施例 3

具体例⑤の染料	2.3%
C. I. ダイレクトイエロー142	0.7%
ジエチレングリコール	15.0%
グリセリン	5.0%
デヒドロ酢酸ナトリウム	0.2%
水	76.8%

#### 実施例 4

具体例⑨の染料	1.8%
C. I. ダイレクトレッド9	0.4%
C. I. ダイレクトイエロー20	0.8%
トリエチレングリコール	10.0%
2,2'-チオジエタノール	10.0%
安息香酸ナトリウム	0.2%
水	76.8%

#### 実施例 5

具体例④の染料	1.9%
C. I. ダイレクトレッド227	0.4%

C. I. ダイレクトイエロー144	0.7%
ポリエチレングリコール 200	5.0%
トリエチレングリコールモノ	
メチルエーテル	15.0%
安息香酸ナトリウム	0.2%
水	76.8%

## 比較例 1

染料 (C. I. ダイレクトブラック32)	3.0%
ジエチレングリコール	15.0%
グリセリン	5.0%
デヒドロ酢酸ナトリウム	0.2%
水	76.8%

## 比較例 2

染料 (C. I. ダイレクトブラック51)	3.0%
ジエチレングリコール	15.0%
グリセリン	5.0%
デヒドロ酢酸ナトリウム	0.2%
水	76.8%

## 比較例 3

染料 (C. I. アシッドブラック28)	3.0%
ジエチレングリコール	15.0%
グリセリン	5.0%
デヒドロ酢酸ナトリウム	0.2%
水	76.8%

表-1 インクの物性

	pH (25℃)	粘度 (c.p.) (25℃)	表面張力 (dyne/cm) (25℃)	*1 耐水性 褪色率 (%)	*2 耐光性 褪色率 (%)
実施例 1	9.8	2.10	50.8	2.8	5.0
" 2	9.7	2.05	50.5	3.4	5.6
" 3	10.1	2.08	52.5	2.8	3.5
" 4	9.8	2.13	50.8	3.7	4.8
" 5	10.0	2.05	51.6	3.8	3.5
比較例 1	9.8	3.50	48.2	6.2	7.0
" 2	10.2	2.82	52.0	7.6	3.7
" 3	10.0	1.95	52.5	28.0	9.5

\*1 インクを純水で染料濃度 1wt% に希釈して上質紙にドクターブレードで塗布し、1日風乾してサンプルを作成した。このサンプルを30℃の水に1分間浸漬した後の濃度をマクベス濃度計で測定し浸漬前の濃度と比較した。

褪色率 = [(浸漬前の濃度 - 浸漬後の濃度) / 浸漬前の濃度] × 100

\*2 \*1と同様にして作成したサンプルを3時間フェードメータ(カーボンアーク灯、63℃)にかけ\*1と同じ方法で褪色率を求めた。

## 効 果

(I) 実施例 1 のインク組成物について、4つの項目について評価試験を行った。その結果を以下に示す。

## 1) 画像鮮明性および画像の乾燥性:

内径30μmのノズルから粒子周波数1100kHzの条件で市場の上質紙上にインクをジェット記録したところ、ニジミのない鮮明な黒色画像が得られた。記録物の乾燥時間は常温常湿で10秒以内であった。

## 2) 保存性:

インクをガラス容器に密閉し、-20℃で1か月間、4℃で1か月間、20℃で1年間、及び90℃で1週間、夫々保存したが、析出は認められなかった。またインク物性や色調についても変化は認められなかった。

## 3) 噴射安定性:

前記 1) のジェット記録を1000時間連続して行なったが、ノズルに目詰りや噴射方向の変化なく、安定した記録が行なえた。

## 4) 噴射応答性:

前記 1) に従ってジェット記録を行なった後、常温常湿で1か月間、及び40℃-30%RHで1週間夫々放置し、ついで再び1)のジェット記録を行なったが、前記 3) と同様、安定した記録が行なえた。

(II) 実施例 2~5 のインクについて実施例 1 と同じく噴射応答性をテストしたところ実施例 1 と同様に良好な結果が得られた。これに対して比較例 1~3 の場合は、常温常湿で1週間、および40℃30%RHで3日間放置したところ、各々ノズルの部分的目詰りが生じてインクの噴射方向が著しく不安定となり、ジェット記録は不可能であった。

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手続補正書 (自発)

昭和60年12月9日

特許庁長官 宇賀道郎 殿

1. 事件の表示

特願昭60-224901号

2. 発明の名称

水性インク組成物

3. 補正をする者

事件との関係 特許出願人

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5. 補正命令の日付 (自発)

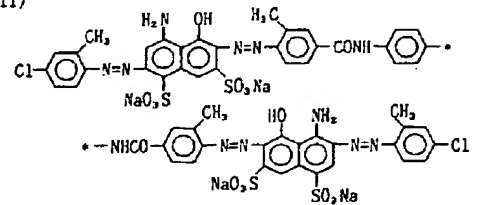
6. 補正の対象

明細書中、発明の詳細な説明の欄

7. 補正の内容

(1) 明細書第11頁の化合物(11)並びに(12)の構造式を下記のとおり訂正する。

(11)



(12)

